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### 1. Introduction

The organic contaminants present in outlet water and environmental air have been bothering us for a long time. In particular, the emissions of volatile organic compounds (VOCs) to the atmosphere are regarded as a great threat to human health.

# Excellent porous environmental nanocatalyst: tactically integrating size-confined highly active $MnO_x$ in nanospaces of mesopores enables the promotive catalytic degradation efficiency of organic contaminants<sup>†</sup>

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The confinement of refined catalytically active substances in special nanospaces is beneficial for promoting reaction processes by taking advantage of the guantum confinement effect and enlarged atomic efficiency. Herein, we present a redox nanoporous molecular sieve nanocatalyst containing sizeconfined active MnO<sub>x</sub> in the siliceous nanospace of mesopores via a functional micelle-assisted in situ embedding strategy. We also demonstrate its excellent environmental catalytic efficiency toward the oxidative degradation of methyl orange in the liquid phase (8 min) and volatile toluene in the gas phase  $(T_{90}/T_{100} = 225/240 \text{ °C}$ , under the mass space velocity of 60000 ml g<sup>-1</sup> h<sup>-1</sup> and concentration of 1000 ppm, which surpass noble metal catalysts and most composite catalysts). This was achieved by virtue of eliminating diffusion limitations, and great active atom-efficiency. In this synthetic strategy, the well-made resultant MnO<sub>x</sub> had a refined size and greater interaction with diffusing reactant molecules without impeding their diffusion and mass transfer. Excellent and durable catalytic efficiency was demonstrated, due to the superior characteristics concerning the great dispersion of MnOx and favorable structure, thereby confirming that high catalytic removal efficiency depends on the amount of accessible  $MnO_x$  rather than the loading of active species. Our findings provide the first example of a heterogeneous environmental catalyst that affords highly efficient catalytic elimination of organic contaminants in both liquid and gaseous systems.

> Therefore, the removal of VOCs in air and large organic molecules in the liquid phase is highly necessary for the protection of the environment and for green chemistry.<sup>1–4</sup> For instance, catalytic combustion treatment of VOCs emerged as an efficacious end-step technique as compared to other processes such as adsorption tactics. The design and development of highlyefficient functional catalysts, especially transition metal-based catalysts are crucial by virtue of the enhancement of reaction activity.<sup>5–9</sup>

> Nanometric space confinement of the heterogeneous reaction process exerts a significant positive effect on the improvement of micromolecule reaction activity, because of the involved molecular diffusion, mass transferring factors and contact activation of reactant molecules.<sup>10–13</sup> Many endeavors have been devoted to this research by creating positive active catalytic species in the confined reaction micro-region, aiming to achieve the high atom utilization of active species. However, the regulation of the size-matched catalytic active species and applicable reaction space for the enhancement of reaction

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activity remains a big challenge during the heterogeneous catalytic reaction, especially for environmental catalysis.

Mesoporous silica has emerged as a promising catalytic nanomaterial, thanks to the excellent surface area and suitable pore size and volume.<sup>14-16</sup> Various active metal species have been contrived for encapsulation in the nanopores of mesoporous silica<sup>17</sup> and the post-impregnation method is still the most widely employed method to achieve this purpose.<sup>18</sup> However, we have noticed that the distribution and position of active metal species are still not well controlled during the post-impregnation process because of the non-uniformity of the active metal species, which easily aggregate under high-temperature driven force.<sup>19,20</sup> Therefore, the atom efficiency of active metals tends to be insufficient. Although some small enough nanoparticles have been confined in the mesopores of silica, the diffusion channels of the original two-dimensional interconnected mesopores might be blocked completely or partially, owing to the presence of metal particles in a certain position. Therefore, one of the reactant molecules has to turn back, or be delayed, when several molecules simultaneously meet at the blocked pore, even missing the chance for contact with other active species, especially for the stream-directed heterogeneous gas-solid reaction. The nanospherelike mesoporous silica is more susceptible to this issue due to the sealing pore in the center of the sphere.<sup>21,22</sup> Therefore, the modification of mesoporous silica nanospheres with metal oxides for achieving high catalytic efficiency is a challenge but is significant for heterogeneous catalysis.

Special techniques like sonication,<sup>23,24</sup> surface modification,<sup>25,26</sup> etc.<sup>27-29</sup> have been proposed to improve the dispersing process and control of active species, but the results remain unsatisfactory as compared to the expectation. For instance, Sun et al.<sup>30</sup> utilized the interface of the P123 micelle and the pore wall of SBA-15 as the confined space to embed the metal precursors by mechanical grinding. The metal species were capable of being encapsulated and were dispersed in a larger reaction space after the thermal process, but some large metal nanoparticles were still located outside the pore, inevitably due to the inexact mechanical process at the nanometric level. Additionally, this process involves significant mechanical energy consumption, thereby wasting energy and adding to the synthetic cost. Another strategy that incorporates isolated metal atoms into the skeleton of silica is capable of avoiding the blocking of mesopores,<sup>31-33</sup> but most of these metal atoms are easily embedded in the internal skeleton of silica due to the similarity of the atom size between the transition metal and silicon, thus preventing real catalytic activity. Hence, the cluster-like metal species seem to be favorable for the decoration of mesopores but is limited by the synthetic method owing to its instability.

Herein, we propose micelle-induced assembly tactics to trigger Mn cations to directly enter the interface of the siliceous wall and micelles through chemical coordination and counterionmedia interactions, which exclude the additional post-introduction process of metal active species (see Scheme 1). Adjustable amounts of Mn precursors were allowed to enter the interface of the siliceous wall and micelle *via* coordination to the micelle surface amino groups based on the coordination-chemical driving-force effect. The metal species interacted strongly with the siliceous wall and were stabilized by the interactions and were thereby dispersed in the cluster-like state. These resulting samples were systematically characterized to identify their physicochemical properties using their corresponding test techniques based on the nanometric level. Ensuingly, the catalytic evaluation of these catalysts was further explored using the catalytic oxidative degradation of MO in the liquid phase by stimulating the generation of sulfate radicals from peroxymonosulfate and toluene in air that typically make up VOCs gas. To our satisfaction, the synthesized optimal 3Mn-MS achieved the best catalytic degradation efficiency  $(T_{90}/T_{100} = 225/240$  °C) of toluene among almost all monometallic Mn-based catalysts, even outperforming most known well-designed multi-metal composite catalysts. In this regard, this study deals with the role of manganese dispersity and content on the catalytic oxidation degradation properties of large organic molecules and VOCs over Mn-bearing siliceous mesoporous molecular sieves.

#### 2. Experimental section

#### 2.1 Chemicals and materials

Dodecyl amine (DDA,  $\geq$  98%), methyl orange (MO), and potassium peroxymonosulfate sulfate (PMS) were commercially obtained from Aladdin. Manganese chloride tetrahydrate (MnCl<sub>2</sub>·4H<sub>2</sub>O,  $\geq$  99%), tetraethylorthosilicate (TEOS, AR), toluene (AR) and methanol (MeOH,  $\geq$  99%) were purchased from Sinopharm Chemical Reagent Co., Ltd. All chemicals were commercially available and were utilized without further purification.

# 2.2 Synthesis of the targeted Mn-bearing nanoporous molecular sieve catalyst

The synthetic process for the  $Mn^{2+}$ -involved assembly of *x*Mn-MS was as follows: DDA (1.85 g, 0.01 mol) was dissolved in a mixed solution, including deionized water (62.5 ml) and ethanol (25 ml), with additional stirring for 30 min at 45 °C. Controlled amounts of MnCl<sub>2</sub>·4H<sub>2</sub>O (1, 2, 3, 4 and 5 mmol) were introduced, and the solution became brown and translucent. TEOS (10.73 ml) was added dropwise under stirring and kept for another 4 h with stirring and was static for 18 h at 45 °C. Finally, the resultant catalyst samples were attained after centrifugation and washing several times with water and ethanol and were then annealed for 6 h at 550 °C in air. The resulting catalysts corresponding to the controlled manganese amounts were labeled as *x*Mn-MS (*x* = 1, 2, 3, 4, and 5), whose Mn/Si molar ratios were in theory 2.08, 4.17, 6.24, 8.32 and 10.4 (%).

#### 2.3 The assessment of catalytic performance and stability

Oxidative degradation of MO in the liquid phase. The catalytic performance of the prepared catalysts was evaluated in the catalytic oxidative degradation of large organic molecules with the assistance of PMS. The reaction was conducted in a 100 ml beaker containing 100 ppm of MO solution at room temperature. A certain amount of PMS (12 mmol  $L^{-1}$ ) was



Scheme 1 (a and b) Synthetic depiction and coordination evidence of the  $Mn^{2+}-N$  group for a highly active porous nanosphere integrated with size-confined  $MnO_x$ .

introduced before the reaction. Afterwards, 40 mg of catalyst was dispersed in the mixture to stimulate the degradation reaction for 60 min in a continuous process. At a certain interval, the concentration of MO was analyzed by virtue of a UV detector. Additionally, to evaluate the stability of the optimal catalyst, the catalyst was collected by centrifugation after one trial for the subsequent cycle testing.

Oxidative degradation of toluene in air. The catalytic oxidative elimination of toluene in the gas phase was conducted using the synthesized Mn-based catalysts in a continuous-flow fixed-bed tubular reactor at atmospheric pressure (Scheme S1, ESI<sup>†</sup>). Specifically, 100 mg of catalyst (40-60 mesh), derived from tableting and sieving, was further mixed with commercial quartz sand (40-60 mesh) and fixed in the reactor filled with the quartz wool plug and equipped with a K-type thermocouple. The reactant gas mixture consisted of 1000 ppm toluene vapor (produced by compressed air bubbling from liquid toluene in a simple ice-water isothermal bath); one stream of air was used as the balance with a total flow rate of 100 ml  $min^{-1}$ , and its weight hourly space velocity (WHSV) was calculated as  $60\,000 \text{ ml g}^{-1} \text{ h}^{-1}$ . The reactor bed was preheated from room temperature to 100 °C prior to each test, with an additional 1 h temperature plateau to prevent overestimation of the toluene conversion; the programmed temperature control was conducted from 180 to 300 °C. The concentration of toluene and possible products involving various reaction temperatures in the outlet were evaluated by an online CEAULIGHT GC 7290 gas chromatograph (Flame Ionization Detector (FID)) under steady-state conditions after 30 min of reaction stabilization.

### 3. Results and discussion

The synthetic strategy, as depicted in detail in Scheme 1, follows the functional micelle-induced self-assembly route *via* 

the coordination of Mn<sup>2+</sup> with the amino surfactant and counterions-media interactions between the negative siliceous oligomers and metallomicelles. The DDA molecules firstly assemble into the micelles with the enriched surface amines that can capture the metal Mn ions through the coordination interactions. This functional Mn<sup>2+</sup>-micelle became the cationiclike micelle liquid-crystal template and easily matched with the negative siliceous oligomers via the counterions media. As a result, the confined  $MnO_x$  species were generated in situ in the nanoporous silica. UV-visible spectra were utilized to identify the variation in the metal ion coordination environment before and after adding DDA molecules, which was evidenced by the presence of an emergent UV absorbance peak at 270 nm (Scheme 1a), indicating the realized coordination effect for the Mn<sup>2+</sup> and DDA molecule.<sup>34</sup> Further direct evidence of the coordination was observed via the color variation of the solution due to the formation of metallomicelles (inset in Scheme 1b).

#### Structural and morphology characterizations

The FESEM technique has been used to determine the microscale morphology and the variation in the regularity of Mn-based series samples; the representative SEM images of several comparable samples are presented in Fig. 1. Typically, the defined nanospherical particles are visibly displayed with regard to each sample, but it is noticeable that the surface state including particle size and spherical regulation show a certain variation on account of the adjustable Mn loading in the assembling procedure. In the case of the low-loading Mn-bearing sample (1Mn-MS and 2Mn-MS), the spherical state of the sample seems far from satisfactory as compared to that of the high-loading Mn-containing sample (3Mn-MS and 4Mn-MS). Specifically, the 3Mn-MS and 4Mn-MS samples have more uniform nanosphere morphologies. This phenomenon absolutely demonstrates the participation of Mn cations in the



Fig. 1 Representative SEM images of various comparable series samples, (a) 1Mn-MS, (b) 2Mn-MS, (c) 3Mn-MS, (d) 4Mn-MS, and (e) 5Mn-MS, and a specific simulated diagram (f).

liquid crystal template assembling procedure for nanoporous silica. It was observed that the over-dosage of Mn in the self-assembly process caused the morphology distortion (5Mn-MS), which favors the above-proposed conclusion.

Transmission electron microscopy is a technique that is used to determine the morphology and microscale structure and provides the greatest evidence for identifying the nanostructural sample. As shown in Fig. 2a–c, the representative nanospherical structures of 3Mn-MS were obviously observed in several typical TEM images, and the relatively uniform size (100–200 nm) of the nanospheres is obvious. Note that the sizeconfined MnO<sub>x</sub> particles failed to be observed based on the selected microscale regions, indicating their ultra-fine size and conceivable cluster-like state in the confined nanopores of silica. However, the existence and presence of Mn species in the mesoporous silica were confirmed based on the elemental mapping results (Fig. 2e), in which the Mn was well dispersed in the selected region. The non-directive porous structure of sample 3Mn-MS was precisely identified, and was in good agreement with the N<sub>2</sub> adsorption/desorption results, beneficial for the diffusion and mass transfer of reactant.

To identify the porous character of the series samples, the low-angle XRD technique was used to examine the resultant samples. As shown in Fig. 3, a typical mesoporous phase 100 diffraction peak located at  $2\theta = ca$ .  $2^{\circ}$  was observed, clearly indicating the mesostructure of the resultant targeted materials.<sup>35,36</sup> The 100 diffraction peak position showed a remarkable shift towards high angle, along with the trend of decreased intensity with gradually-increasing Mn concentration in the catalyst, demonstrating the decreasing  $d_{100}$  space distance and damage to the mesostructure to some extent. This is associated with the fact that Mn ions participate in the assembly process for mesoporous silica<sup>20,37</sup> and the gradual insertion of MnO<sub>x</sub> in molecular sieves.

The porous properties were determined using N2 adsorption/ desorption isotherm measurements. The typical IV type curve for these samples is presented in Fig. 4a, which is in accordance with that of typical mesoporous materials.<sup>38</sup> However, the curve gradually transformed to type I-like behavior with the enhanced Mn loading in the mesochannel, verifying the appearance and enrichment of micropores owing to the aggregation and occupation of  $MnO_x$  species in mesochannels. The pore size distribution calculated from the BJH model also reconfirmed the decreasing trend of pore size because of the occupation of more MnO<sub>x</sub> species in the mesochannel. The detailed textural parameters are displayed in Table 1, thus, the increase in pore wall thickness with the increasing Mn loading can be clearly observed, further indicating the adhesion of MnO<sub>x</sub> species on the pore wall (Scheme 2).<sup>34,39</sup> These results demonstrated the introduction and confinement of cluster-like MnO<sub>x</sub> species in mesochannels. However, what we noticed was the disappearance of mesopores, especially for the 4Mn-MS and the 5Mn-MS to some extent, indicating the possible blocking and closing of pores after over-introducing MnO<sub>x</sub> species.



Fig. 2 (a-c) Representative TEM images of 3Mn-MS; (d) specific simulated diagram and (e) its SEM-EDX elemental mapping results; scale bar 1  $\mu$ m.



**Fig. 3** Low-angle XRD patterns of a series of Mn-based mesoporous molecular sieve samples *x*Mn-MS.

Wide-angle XRD was utilized to ascertain the crystal state of the whole material and the probable phase state of active Mn species; their corresponding pattern results involving uncalcined and calcined catalysts are displayed in Fig. 5a and b. As observed, the broad diffraction peak ranging from  $20-30^{\circ}$ is attributable to the amorphous siliceous carrier.<sup>40</sup> A weak swell at  $35^{\circ}$  was identified in the case of the high concentration Mn-bearing samples(Fig. 5b) and was assigned to the lowcrystalline degree of size-confined MnO<sub>x</sub> species (Mn<sub>3</sub>O<sub>4</sub>, PDF# 24-0734) inside the nanopores of mesoporous silica.<sup>41</sup> To probe the state of Mn species in the as-synthesized Mn-containing series samples, we identified the uncalcined samples using the wideangle XRD technique (Fig. 5a). The results demonstrate the consistent crystalline state of the siliceous support before and after calcination. Besides, the crystalline state of  $MnO_x$  was not detected in the curves of the uncalcined samples, signifying the oxidative ions state of Mn in the interface between the siliceous wall and micelles of initial as-synthesized samples.

To determine the presence and coverage of the introduced MnO<sub>x</sub> on the siliceous surface, the FT-IR spectra ranging from 990 cm<sup>-1</sup> to 880 cm<sup>-1</sup> of these resultant series catalyst samples of xMn-MS are presented in Fig. 6a. The variations in the intensity of the peak at 956 cm<sup>-1</sup> (due to surface Si–OH groups) were obviously discerned with the enhanced loading of MnOr on the surface. The gradual decrease in intensity with the gradual incorporation of MnO<sub>r</sub> species on the siliceous surface is regarded as the specific evidence for the consumption of surface silanol groups, owing to the strong chemical interaction between the inherent surface silanol groups and MnOr species.<sup>42</sup> In addition, the coverage of MnO<sub>x</sub> on the surface of the siliceous (Fig. 6b) wall was further identified based on the calculation of the numbers of Si-OH groups, in light of the decreased intensity of the IR absorption peak and their respective surface areas (Fig. 6c and Table 1). In contrast, the interacting Si-OH group numbers of 3Mn-MS accounted for the biggest proportion despite the higher loading of MnO<sub>r</sub> in 4Mn-MS and 5Mn-MS, thus indicating its highest exposed degree of introduced unit MnO<sub>x</sub> species (normally, the number of Si-OH groups is demonstrated for *ca.* 4 per nm<sup>2</sup>).<sup>43</sup>



Fig. 4 (a) N<sub>2</sub> adsorption/desorption isotherms and (b) pore size distribution of series xMn-MS molecular sieve samples.

 Table 1
 Textural properties and parameters of series Mn-bearing porous silica samples

Samples	Mn (%)	$S_{\rm BET}  ({ m m}^2  { m g}^{-1})$	$V_{\rm a} \left( {\rm cm}^3 {\rm g}^{-1} \right)$	$D_{\rm p}^{\ a}  ({\rm nm})$	$a_0^b$ (nm)	$d_{100}{}^{c}$ (nm)	$d_{\mathrm{W}}^{d}$ (nm)
Pure HMS	0	868	0.78	3.49	4.96	4.30	1.47
1Mn-MS	2.2	862	1.08	2.73	5.30	4.59	2.57
2Mn-MS	4.1	814	0.72	2.44	5.10	4.39	2.66
3Mn-MS	6.2	800	0.54	2.14	4.70	4.07	2.56
4Mn-MS	7.5	466	0.29	1.58	4.59	3.98	3.01
5Mn-MS	8.2	380	0.61	1.57	_	_	_

 ${}^{a}_{c} D_{p}$  represents the most probable pore size from the BJH pore size distribution.  ${}^{b}_{a_{0}}$  represents the unit cell parameter,  $a_{0} = 2d_{100}/\sqrt{3}$ .



Scheme 2 Description of the introduction of  $MnO_x$  species into the mesopores of the siliceous molecular sieves.

DRUV-vis spectra (Fig. 7a) were utilized to further identify the metallic state of the introduced Mn species on the surface of the siliceous pore wall. To our knowledge,  $Mn_3O_4$  can be recognized as a type of  $Mn_2O_3$ ·MnO. Specifically, the two bands near 311–323 nm are ascribed to the charge transition  $(O^{2-} \rightarrow Mn^{3+})$  in  $Mn_3O_4$ , where octahedral Mn coordinates with oxygen. The second band centered at *ca.* 512 nm corresponds to the crystal field transition of  $Mn^{2+}$  ( $6A_{1g} \rightarrow 4T_{2g}$ ) as observed in  $Mn_3O_4$  and  $MnO.^{44,45}$  Thus, these two broad bands at around 311–323 and 512 nm in the DR UV-vis spectra of *x*Mn-MS demonstrate the coexistence of  $Mn^{2+}$  and  $Mn^{3+}$ . The weak shoulders at around 359 nm could be attributed to d–d transitions of the  $5B_{1g} \rightarrow 5B_{2g}$  and  $5B_{1g} \rightarrow 5E_g$  of  $Mn^{3+}$  in  $Mn_2O_3$ , and the weak peak at around 616 nm corresponds to the  $6A_{1g} \rightarrow 4T_{2g}$  transition of  $Mn^{2+}$  in MnO. Taken together, the evidence indicates the presence and state of the size-confined  $MnO_x$  in  $Mn_3O_4$ .

The direct association of the reducibility of the transition metals with catalytic activity was further indicated by a H<sub>2</sub> temperature-programmed reduction process technique (H<sub>2</sub>-TPR). Fig. 7b presents the H<sub>2</sub>-TPR profiles of the series catalysts. One visual peak, ascribed to the reduction of the Mn species (Mn<sub>3</sub>O<sub>4</sub>  $\rightarrow$  MnO), was observed at *ca.* 350 °C,<sup>46</sup> corresponding to the weak interaction of MnO<sub>x</sub> on the porous wall, which accounts for MnO<sub>x</sub> species introduced with relatively lower reducibility. In contrast, the remarkable shift from the reduction peak of Mn<sub>3</sub>O<sub>4</sub> at the higher temperature (*ca.* 420–550 °C) is ascribed to the strong interaction between MnO<sub>x</sub> and the siliceous wall, associated with the higher redox capacity.<sup>26</sup> Notably, Mn-bearing 3Mn-MS with two adjacent reduction peaks correspond to the above-mentioned



Fig. 5 Wide-angle XRD patterns of uncalcined (a) and calcined (b) series of xMn-MS catalyst samples.



Fig. 6 (a) FTIR spectra of xMn-MS samples; (b) schematic description of the surface status of  $MnO_x$  on the siliceous wall; (c) coverage degree and calculated area of coverage of  $MnO_x$ .



Fig. 7 Diffuse UV-vis spectra (a) and  $H_2$ -TPR profiles (b) of xMn-MS samples.

two kinds of  $MnO_x$ . However, interestingly, the  $MnO_x$  ascribed to stronger redox ability in 3Mn-MS has the highest proportion as compared to its counterparts, despite the greater loading of Mn in 4Mn-MS and 5Mn-MS.

To identify the chemical environment of the various elements in the catalysts, the uncalcined HMS-DDA, u-3Mn-MS, and calcined 3Mn-MS were determined by the high-resolution XPS technique. Fig. 8 presents XPS spectra of N1s (Fig. 8a), Mn2p (Fig. 8b), and O1s (Fig. 8c) in the u-3Mn-MS and 3Mn-MS. For Mn2p spectrum of u-3Mn-MS,  $Mn2p_{1/2}$  and  $Mn2p_{3/2}$  with the binding energy value at 642 eV and 654 eV, respectively. For the sample of 3Mn-MS,  $Mn2p_{1/2}$  and  $Mn2p_{3/2}$  correspond to the binding energy of 641.65 eV and 653.95 eV respectively, agreeing with the typical  $Mn_3O_4$  species.<sup>47</sup> The binding energies of Mn2p before and after calcination showed an obvious shift (0.35 eV) related to the transformation of metal atoms from ionic status to the metal oxide phase. This phenomenon indicates that the metal species underwent surface-interactions on the pore wall rather than forming a stable framework.

Additionally, the coordination decoration and interaction of Mn ions on N groups of DDA micelles in the resultant sample are further ascertained using the XPS spectrum of N1s core



Fig. 8 XPS spectra of (a) N1s, (b) Mn2p, and (c) O1s core levels, and (d) full survey of several comparable samples including calcined 3Mn-MS and uncalcined u-3Mn-MS samples.

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level (Fig. 8a). The N1s spectrum of uncalcined DDA-bearing HMS showed a dominant peak with binding energy of 399.60 eV, and a shoulder at 401.3 eV corresponding to the free amino moiety that interacted with the siliceous wall by hydrogen-bonding in the DDA molecule.48 In contrast, u-3Mn-MS showed two characteristic N1s peaks at 399.5 and 401.7 eV, where the binding energy of 401.7 eV differs from that previously mentioned for interactions by hydrogen-bonding. The obvious shift (0.4 eV) to high binding energy and the obviously-enhanced intensity were observed, which indicated the variation in N atoms in the chemical state and coordination environment before and after introducing Mn<sup>2+</sup> into the assembly process. In addition, the obvious decrement in the amount of free amino groups because of the introduction of Mn ions was evidenced by the increased peak intensity of nitrogen atoms interacting with Mn ions, which was strongly attributed to the Mn<sup>2+</sup> coordinated to the N atoms of the DDA molecule where the electron-enriched nitrogen atoms shared electrons with Mn ions, thereby resulting in the lowered electron density of the nitrogen atoms.49 Additionally, the existence and absence of the N1s peak in the u-3Mn-MS and 3Mn-MS XPS survey spectra verified the removal of surfactant template by calcination.

#### Catalytic analysis

The catalytic activity of the  $MnO_x$ -cluster-embedded nanoporous silica was systematically evaluated using the oxidative degradation process of MO aqueous solution. Herein, peroxymonosulfate emerges as the oxidant agent, which has been demonstrated to be oriented over the functional active sites of mesoporous silica. The oxidative sulfate radicals ( $SO_4^{\bullet-}$ ) possess higher oxidation electric potential (2.5–3.1 eV) with respect to hydroxyl radicals (2.7 eV), which is beneficial for accelerating the oxidation reaction process.<sup>50</sup> On the other hand, the catalytic active sites are regarded as the promotive factors, with the conductive cluster-like  $MnO_x$  affording more exposed active centers in the pores, which is beneficial for enhancing the catalytic activity.

We performed the degradation test using the series of Mn-functionalized molecular sieve samples under identical reaction conditions (Fig. 9). The reaction process of MO degradation involving 1Mn-MS at different times was determined (Fig. 9a). Before the degradation, we assessed the catalytic performance of the pure HMS sample in the MO aqueous solution, which gave a feeble catalytic activity for the oxidation degradation in the absence of the PMS (Fig. 9b). The results demonstrated that the catalytic activity should be mainly derived from the Mn species. On the other hand, the *x*Mn-MS catalysts showed evolutive catalytic performance (Fig. 9b and c) corresponding to the variation in reaction time under identical reaction conditions, which is associated with the different physicochemical states of catalysts. Note that the catalytic activity affords an interesting variational trend with increased Mn-loading in silica, in which the catalytic performance was enhanced from the 1Mn-MS to 3Mn-MS, while a decreased trend in catalytic activity was demonstrated as the Mn loading was further raised to 8.32% (Mn/Si). In conjunction with the aforementioned characterizations, we suggest that the MnO<sub>x</sub>

might cause obvious aggregation and block in the mesopore to some extent, with more and more Mn species appearing on the pore surface. Additionally, the excessive introduction of Mn species in the nanopores of silica obviously destroyed the porous structure, which gave rise to the physical structural properties. In particular, we observed that the mesoporous diffraction peak of sample 5Mn-MS almost disappeared at  $2\theta = \sim 2^{\circ}$ , indicating the absence of regular mesopores in the resulting samples. The MnO<sub>r</sub> species were embedded in closed pores without the real exposed active sites that can come in contact with the reactants in the reaction system. Therefore, the 3Mn-MS afforded the appropriate TOF value as compared to other counterparts at relatively high metal loading (Fig. 9e), based on the comprehensive consideration of Mn loading and reaction conversion rate. On the other hand, according to the  $H_2$ -TPR results, the surface  $MnO_x$  species afforded different states corresponding to discriminative reduction temperatures. In particular, the surface interacted MnO species in the 3Mn-MS took up an obviously large proportion as compared to that of other Mn loading samples. We also observed that the 3Mn-MS afforded the highest catalytic activity, which may be due to the surface interacted MnO<sub>x</sub> species.

We proceeded to evaluate the catalytic stability of the selected optimal catalyst *via* recycling the used catalyst; the catalytic results are presented in Fig. 9d. To our delight, the catalytic activity was retained for at least 5 cycles. In view of the slight drop in the catalytic activity, we checked the Mn content retained in the catalyst using the ICP measurements. The leaching of the Mn element was observed from 6.2 wt% to 5.1 wt%, which should account for the loss of catalytic activity after recycling several times.

$$\mathrm{Mn}^{2^+} + \mathrm{HSO}_5^- \rightarrow \mathrm{Mn}^{3^+} + \mathrm{SO}_4^{\bullet-} + \mathrm{OH}^-$$
(1)

$$Mn^{3+} + HSO_5^{-} \rightarrow Mn^{4+} + SO_4^{\bullet-} + OH^{-}$$
(2)

$$Mn^{3+} + HSO_5^{-} \rightarrow Mn^{4+} + SO_4^{2-} + {}^{\bullet}OH$$
(3)

$$Mn^{4+} + HSO_5^{-} \rightarrow Mn^{3+} + SO_5^{\bullet-} + H^+$$
(4)

 $Mn^{(3+/4+)} - OH + HSO_5^- \rightarrow Mn^{(3+/4+)} - HSO_5^- + OH^-$  (5)

$$Mn^{(3+/4+)} - HSO_5^{-} + 2H_2O \rightarrow Mn^{(3+/4+)} - OH^{-} + SO_4^{\bullet^{-}} + O_2 + 4H^{+}$$
(6)

$$\mathrm{SO}_4^{\bullet-} + \mathrm{OH}^- \to \mathrm{SO}_4^{2-} + {}^{\bullet}\mathrm{OH}$$
 (7)

$$2^{\bullet}OH + SO_5^{-} \rightarrow SO_4^{\bullet-} + H_2O + O_2$$
 (8)

Based on the reported literature, we tentatively speculate that the formation (Scheme 3) of oxidative radicals, including sulfate radicals and hydroxyl radicals, is derived from the transformation of  $Mn^{2+}$  and  $Mn^{3+}$  into  $Mn^{4+}$  species of surface  $MnO_x$ , which is thermodynamically favorable for activating  $HSO_5^{-}$  by  $Mn^{2+}$  and  $Mn^{3+}$  to generate active •OH and  $SO_4^{\bullet-}$ , referring to eqn (1)–(3).<sup>51,52</sup> In the meantime,  $Mn^{4+}$  was changed back into  $Mn^{3+}$ , accompanied by the generation of  $SO_5^{\bullet-}$  by reacting with  $HSO_5^{-}$  (eqn (4)).<sup>53,54</sup> Thus, the hydroxyl species produced in eqn (1) and (2) as well as those from the dissociation of physically adsorbed  $H_2O$  molecules could bind to the surface of

Paper



Fig. 9 (a) The catalytic degradation of MO using 1Mn-MS as displayed by dynamic UV spectra. (b and c) Catalytic degradation performance of comparable catalysts, and (d) the recycling test results of 3Mn-MS. (e) TOF values of the involved comparable samples, and (f) EPR spectra of 2Mn-MS and 3Mn-MS (reaction conditions are as follows: 10 ppm DMPO, 20 ppm MO, 0.1 g L<sup>-1</sup>, 1 mM PMS, pH of 7, 25 °C, and reaction time of 5 min).

 $Mn^{(3+/4+)}$  sites of the catalyst to generate  $Mn^{(3+/4+)}$ -OH, which would then interact with HSO<sub>5</sub><sup>-</sup> by ligand displacement to form  $Mn^{(3+/4+)}-HSO_{5}^{-}$  (eqn (5)). Afterward,  $Mn^{(3+/4+)}-HSO_{5}^{-}$  dissociated into  $SO_4^{\bullet-}$  in eqn (6).<sup>55</sup> Partial •OH was also produced by reacting  $OH^{-}$  and  $SO_{4}^{\bullet-}$  (eqn (7)). In the meantime, some  $\bullet OH$  induced by  $SO_5^-$  resulted in  $SO_4^{\bullet-}$  in eqn (8).<sup>56,57</sup> To confirm the presence of both  ${}^{\bullet}OH$  and  $SO_4 {}^{\bullet-}$  radicals, EPR spectral studies were performed and are displayed in Fig. 9f. As expected, the 'OH and  $SO_4^{\bullet-}$  signals were recognized as the specific evidence for affirming the proposed mechanism process. Additionally, the intensity of signals for the tested 3Mn-MS and 4Mn-MS further sustained the active site numbers-determined catalytic performance.

Apart from the above study concerning the liquid oxidation degradation of MO, the catalytic capacity of the Mn-based

catalyst in toluene combustion in air was further assessed to explore its potential in VOC treatment. Before the catalytic experiment, the adsorption of toluene on the resultant Mn-bearing catalysts was firstly measured on the basis of the pressure-swing process, as shown in Fig. 10a, which could indicate the diffusing behavior of toluene in the real catalyst's pore. As a result, the variation in the adsorption amount in view of the increased Mn loading could be observed clearly, implying the rational decrement due to the progressive introduction of  $MnO_x$  species into the reaction channel. In particular, the observation of the capillary condensation around  $P/P_0 \sim 0.2$ with regard to the 1Mn-MS, 2Mn-MS, and 3Mn-MS verified the normal mesoporous channel without complete blocking after the controlled introduction of Mn species.<sup>58</sup> However, the loss of toluene adsorption in the 4Mn-MS and 5Mn-MS is



Scheme 3 Schematic catalytic oxidative degradation of MO in aqueous solution.



Fig. 10 Toluene adsorption isotherms of a series of Mn-based catalyst (a), the catalytic degradation efficiency of toluene using a series of Mn-based catalysts (b). Arrhenius plots of 3Mn-MS, 4Mn-MS, and 5Mn-MS (c), and life test of catalyst 3Mn-MS under the optimal reaction conditions (d).

remarkable as compared to several other counterparts. This indicates the possible closing and blocking of reaction channels in the presence of larger toluene molecules, which is in good agreement with previous characterization analyses. The greater adsorption capacity of 5Mn-MS compared to 4Mn-MS could be due to the greater packing porosity among interparticles rather than mesopores, which agrees well with the N<sub>2</sub> adsorption/desorption results.

The catalytic oxidative degradation of toluene over all of the samples in the fixed-bed reactor was evaluated in the range

from 180–300 °C, which is displayed in Fig. 10b. The scalariform increment in catalytic performance is clearly observed with increased reaction temperature. However, the reaction trend in the presence of the increasing loading of Mn species gives rise to a similar phenomenon to the above liquid reaction systems, which is associated with the pore blocking of excessive  $MnO_x$  species. This can further account for the higher catalytic efficiency of 3Mn-MS as compared to other counterparts because of the best degree of exposure of the active substance on the external surface coupled with the unplugged diffusing channel. Note that the pristine catalytic conversion of toluene before 180 °C was still observed below 40%, implying that there was catalytic progress even at a lower reaction temperature; however, the catalytic efficiency was undesirable from a practical point of view. The dramatic enhancement in catalytic conversion was demonstrated after 200 °C, especially for the 3Mn-MS, which was directly related to the more accessible active centers that appeared on the catalyst. Apart from the produced H<sub>2</sub>O molecules, according to the GC results, CO<sub>2</sub> emerged as the only product at 240 °C. However, at a lower temperature, CO was partially visible, and other intermediates were weak or absent. As a result, the  $T_{90}$  and  $T_{100}$  can be achieved at 225  $^\circ C$  and 240  $^\circ C,$  which is far superior to several other comparable catalysts. Notably, the catalytic efficiency of these used catalysts follows the sequence: 3Mn-MS > 4Mn-MS >5Mn-MS > 2Mn-MS > 1Mn-MS. To our delight, when compared to the reported catalyst systems (Table 2), the superior catalytic efficiency of 3Mn-MS was the most outstanding current monometal-bearing Mn-based catalyst, even higher than those well-designed composite catalysts obtained by incorporating multiple active metal centers.

To ascertain the catalytic stability and life of the resultant optimal catalyst, the catalytic assessment was carried out over 600 min under identical reaction conditions, and the near 100% conversion activity in the successive catalytic cycles indicates the durable catalytic performance in the present catalytic system. To explain the existing promotive catalytic efficiency of 3Mn-MS in toluene conversion, in conjunction with the aforementioned toluene adsorption results, we propose the possible efficient catalytic model based on the diffusioneliminated pathway (Scheme 4b) as compared to its counterpart with the pore-blocked catalyst (Scheme 4a). This is associated with the fact that the blocked pore fails to accommodate the unidirectional flow of the toluene reaction molecule under high space velocity, and the back-mixing effect cannot exist in the gassolid phase reaction, unlike the interim liquid phase reaction.

At a more fundamental level, this catalytic process followed a first-order reaction mechanism with respect to toluene concentration, which has been affirmed by wide investigations.<sup>70</sup>

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Scheme 4 Illustration of the encouraging catalytic diffusion reaction pathway in catalytic toluene degradation in a fixed-bed reactor using unidirectional airflow: (a) blocked diffusion channel; (b) free diffusion channel.

The apparent activation energies ( $E_a$ ) calculated by the Arrhenius plots for the three samples with advantageous activity, including 3, 4, 5Mn-MS, were further introduced to evaluate the catalytic activity for these samples, and are presented in Fig. 10c. Specifically, note that the  $E_a$  values follow the order: 3Mn-MS (45.3 kJ mol<sup>-1</sup>) < 4Mn-MS (64.1.8 kJ mol<sup>-1</sup>) < 5Mn-MS (85.4 kJ mol<sup>-1</sup>). Obviously, the  $E_a$  values follow an inverse trend with respect to the catalytic activities. The results clearly indicate that the differences in the  $E_a$  values are most likely related to the differences in the number of active surface sites on the catalyst.<sup>70</sup>

Finally, the real adsorption process of surface-adsorbed species after introducing toluene and the ensuing catalytic reaction process of toluene combustion were understood by virtue of *in situ* DRIFTS experiments performed over the 3Mn-MS catalyst. As shown in Fig. 11a and b, the *in situ* adsorption process of toluene on the active  $MnO_x$  centers was clearly observed and identified by the changing spectra of toluene at 1543 cm<sup>-1</sup> corresponding to the skeletal C–C stretching vibration of the aromatic ring. Before introducing oxygen, the relatively pure spectral characteristics of toluene adsorption were

100

200

240

100

100

100

Take 2 companion of the eatilyte degradation of totache, based on various known eatilysts and own ma						
Catalysts	Conv. tem. (°C)	Initial concentration (ppm)	Dosage (mg)			
Mn <sub>4</sub> Al <sub>0.7</sub> Zr <sub>0.5</sub> Ce <sub>0.1</sub> (im)/CTA-L	$T_{90} = 250$	500	500			
$Cu_{1.5}Mn_{1.5}O_4$	$T_{100} = 270$	1000	350			
OMS	$T_{90} = 311$	1000	100			
$Mn_3O_4$	$T_{90} = 270$	1000	400			
Mn <sub>2</sub> O <sub>3</sub>	$T_{90} = 274$	1000	100			
LaMnO <sub>3</sub>	$T_{90} = 320$	1000	100			
CuMn/La-4 mol%	$T_{90} = 255$	1000	—			
$Ce_{0.03}MnO_x$	$T_{100} = 225$	1000	300			

Table 2 Comparison of the catalytic degradation of toluene, based on various known catalysts and 3Mn-MS

 $T_{90} = 258$ 

 $T_{100} = 240$ 

 $T_{90} = 267$ 

 $T_{90} = 235$ 

 $T_{100} = 270$ 

 $T_{90} = 240$ 

 $T_{90}/T_{100} = 225/240$ 

LaMnO<sub>3</sub>/δ-MnO<sub>2</sub>

Mn/R-SBA-15

Co1.5Mn1.5O4

Co-Mn BHNCs

 $Mn_xZr_{1-x}O_2$ 

Pd-Al<sub>2</sub>O<sub>3</sub>

3Mn-MS

1000

1000

1000

1000

1000

1000

500



Fig. 11 Time-dependent *in situ* DRIFTS 2D (left) and 3D (right) spectra of toluene adsorption over 3Mn-MS (a and b), after inputting 20% O<sub>2</sub>/N<sub>2</sub> at 225 °C for the identification of toluene degradation in the different time courses (c and d).

observed (Fig. 11a), and the adsorption process almost reached saturation after 10 min of dynamic adsorption, indicating the rapid completion of toluene adsorption by the high exposure of surface  $MnO_x$  and its accessibility. Besides, the C=O stretching vibration (1718 cm<sup>-1</sup>) attributed to benzaldehyde was synchronously identified, accompanied by the presence of toluene,<sup>71</sup> and increased by the additional time, which was associated with the surface oxygen-participated oxidation process derived from the catalyst. Note that the other detectable product is sightless, indicating no occurrence of the successive deep oxidation. After the long purge of N<sub>2</sub> at the realized reaction temperature, the physically-absorbed toluene was removed to exclude the interruption of free toluene molecules for the ensuing reaction process. The in situ spectra of toluene adsorption after inputting 20% O<sub>2</sub>/N<sub>2</sub> are further shown in Fig. 11c and d for ascertaining the toluene degradation under the optimal reaction condition. As expected, relatively complex IR spectra were obtained owing to the reaction proceeding after the introduction of sufficient oxygen. A significant decrement in intensity corresponding to the skeletal C-C stretching vibration of toluene was demonstrated, indicating the degradation of toluene in 12 min, thereby accounting for the excellent catalytic capacity of surfaceincorporated  $MnO_x$  through the proposed tactical integration. In addition, the symmetric vibration of the carboxylate band (1383 cm<sup>-1</sup>) was clearly discerned, further indicating the proceeding of successive deep oxidation from the benzaldehyde to the subsequent benzoate and so on. This result also explains the different oxidation mechanisms of toluene derivatives for the demand of oxygen at different oxidative steps during the whole degradation process. Specifically, the toluene molecule was firstly oxidized to benzaldehyde by the surface oxygen derived from  $MnO_x$ , and then further oxidized to benzoate and other deep-oxidized products with the assistance of introduced external oxygen, which is in accordance with some recent reports.<sup>72</sup>

### 4. Conclusions

In summary, we successfully developed a fine-sized MnO<sub>x</sub>modified nanoporous functional siliceous molecular sieve heterogeneous catalyst through the in situ embedding of cluster-like MnO<sub>r</sub> species into mesochannels during the catalyst assembly process. The confined MnOx species were of ultra-tiny size and had strong interactions with the siliceous surface, and the porous siliceous materials showed nanospherical morphology with the assisted assembly process of Mn ions and were influenced by the introduced Mn concentration in the samples. Furthermore, the pore size of the siliceous material was tailored gradually on account of the encapsulation and occupation of MnO<sub>r</sub> clusters in the mesochannel. As a result, the oriented functional catalysts affording the confined MnO<sub>x</sub> active species demonstrated excellent catalytic activity for motivating peroxymonosulfate to oxidatively degrade MO (within 8 min), and the thermal catalytic degradation of toluene  $(T_{90}/T_{100} = 225/240 \ ^{\circ}C)$  in air, superior to most known composite catalysts. This provides significant insight into the environmental catalytic process by virtue of efficient catalyst-design engineering.

## Conflicts of interest

There are no conflicts to declare.

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